GEOCHEMICAL MODELLING OF WATER-ROCK INTERACTION IN CO_2 STORAGE GEOLOGICAL RESERVOIRS: THE WEYBURN PROJECT (CANADA) AS CASE STUDY

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INTRODUCTION

Decreasing the discharge of the anthropogenic CO_2 to the atmosphere is considered an essential step in the control of the global warming. The most effective way to reduce CO_2 emissions at short time is to dispose this green-house gas in deep geological formations (> 800 m): i) saline aquifers, ii) depleted oil and gas fields and, iii) unexploitable coal beds (Holloway, 1997). Once injected, CO_2 can be retained underground in four ways, such as: a) supercritical fluid into a geologic structure (physical trapping), b) $CO_{2(aq)}$ dissolved in an aquifer due to very long flow path (hydrodynamic trapping), c) $CO_{2(aq)}$ dissolved into ground waters (solubility trapping), and d) precipitation of secondary carbonates (mineral trapping: Gunter *et al.*, 1993).

The appealing concept that CO_2 could be permanently sequestered in the subsurface has prompted several experimental studies in Europe and North America sponsored by IEA GHG R&D, EU and numerous international industrials and governments to investigate this process. Among these the most important project is the *International Energy Agency (IEA) Weyburn CO_2 Monitoring & Storage*, an EnCana's CO_2 injection EOR project at Weyburn (Saskatchewan, Canada).

Owing to the possible risks associated to this technique, numerical modelling of geochemical processes is a necessary tool for investigating the short- to long-term consequences of CO_2 storage. In the framework of a collaboration project between the Istituto Nazionale di Geofisica e Vulcanologia of Rome (INGV) and the Department of Earth Science of Florence, the main goal of this work has been that to propose a geochemical model capable of reconstruct the reservoir chemical composition on the basis of surface analytical data and simulate the reservoir evolution subjected to CO_2 injection. The Weyburn Project was chosen as case study to test our model.

To perform our investigation, the PRHEEQC (V2.11; Parkhurst & Appelo, 1999) Software Package via thermodynamic corrections to the code default database (phreeqc.dat) has been used in order to obtain a more realistic modelling. The main modifications to improve the Software Package for our purposes are: i) addition of some solid phases, such as dawsonite, magnesite, epsomite and K-alum, ii) use of P > 0.1 Mpa, iii) variation of the CO_2 supercritical fugacity and solubility (Duan *et al.*, 1992; Duan & Sun, 2002) under reservoir conditions, and iv) addition of kinetic rate equations of anhydrite, chalcedony, kaolinite, dolomite disordered, gypsum, K-feldspar, muscovite, clinochlore, albite, pyrite, magnesite (*e.g.*, Palandri & Kharaka, 2004) and v) calculation of reaction surface area. The thermodynamic data were selected in order to maintain an internal coherence of the whole data set, by selecting only thermo-chemical measurements and, when possible, values pertaining to the same research team, due to the high variability of the available data, *e.g.* dolomite Ksp (Sherman & Barak, 2000).

GEOLOGICAL OUTLINES AND CO_2 STORAGE AT THE WEIBURN OIL FIELD

The Weyburn oil field, located approximately 130 km SE of Regina, Saskatchewan (Canada), is recovered from Midale Beds of the Mississippian Charles Formation (at the depth of 1300-1500 m). This formation consists of shallow marine carbonate-evaporites that can be subdivided into two units: i) the tight dolomitic "Marly" and ii) the underlying calcitic "Vuggy", sealed by an anhydrite cap-rock (Fig. 1).

Presently, more than 3 billions mc of supercritical CO_2, captured from the North Dakota Gasification Power Plant, have been injected into the "Phase A1" injection area that includes about 90 oil producers, 30 water injectors and 30 CO_2 injection wells, built up since September 2000 (*e.g.* Wilson & Monea, 2004). After completing this EOR (Enhanced Oil Recovery) operation, in 2025-2030, it has been

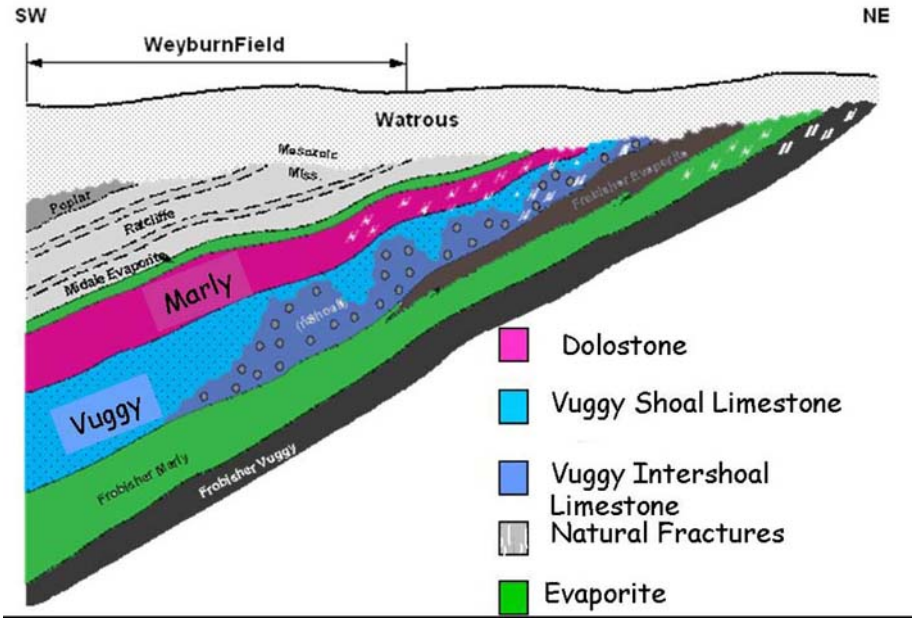

Fig. 1 - Schematic SW-NE geological cross-section of Midale Beds; the carbonate strata of oil reservoir are sealed by evaporite beds and by the Mesozoic Watrous Formation. Modified by Wilson & Monea (2004).

estimated that 15-20 Mt of anthropogenic CO_2 will be stored in the Mississippian strata, with the production of 130 million barrels of oil.

The INGV, jointly with the University of Calgary (Canada), have carried out a full geochemical monitoring program -approximately thrice yearly- from pre-injection trip ("Baseline" trip, August 2000) to September 2004. In this period more of 500 waters were sampled, at head well, in order to analyze the dissolved gases, major and minor elements, strontium isotope ratios and trace metals. The merged experimental data are the base of the present geochemical modeling.

RECONSTRUCTION OF THE *IN-SITU* RESERVOIR COMPOSITION (62°C, 15 MPA)

In the past, assumptions and gap-acceptance have been made in the literature in the frame of the geochemical modeling of CO_2 geological storage, in order to reconstruct the reservoir conditions

(pressure, *p*H, chemistry, and mineral assemblage). The thermodynamic affinity of natural waters with respect to most solid and gases phases is largely controlled by *p*H. Consequently, precise knowledge of the *p*H is a prerequisite for the investigation on mineral solution equilibrium. As most part of strategic geochemical parameters of deep fluids cannot always be measured *in-situ* and at low cost, this information as a whole must be computed by *a posteriori* procedure involving as input the experimental semi-reliable analytical data. In this work we have developed a new approach to geochemical modeling capable of to reconstruct the in-situ reservoir chemical composition (T, P, boundary conditions and *p*H) by using surface data.

Our geochemical modeling procedure is based on the available data of Weyburn Project (*e.g.* Wilson & Monea, (2004), such as:

a) bulk mineralogy of the Marly (80% dolomite, 14.5% calcite, 3% gypsum, 1.25% K-feldspar, 0.5% chalcedony, 0.5% pyrite, and 0.25% kaolinite) and Vuggy (93.5% calcite, 3% dolomite, 2% anhydrite, 0.5% chalcedony, 0.5% pyrite, and 0.5% K-feldspar) units;

b) mean gas-cap composition at the well-heads (43.8% CH_4, 4% CO_2, 22% N_2, 1.3% H_2S, 0.001% H_2, and 0.059% H_2O)

c) selected pre- and post-CO_2 injection water samples from the Marly and Vuggy (7 and 5 water, respectively) units, minimizing the effects of the past 30-years of water flooding in the oil field.

The in-situ reservoir composition was calculated by the thermodynamic equilibrium among the various phases at reservoir temperature (62°C) and pressure (15 MPa). From surface to reservoir Ca and Mg concentrations decrease due to carbonate precipitation, pH slightly increases from 6.55 to 6.70, while HCO_3 concentration remains unchanged. Because of the low Eh measured (*i.e.* -0.25 V) gypsum and anhydrite dissolve and SO_4 reduces to HS. The variability of Si and K depends on both dissolution of K-feldspar and precipitation of chalcedony and kaolinite. Finally, Na, Cl and Li values remain unchanged (Fig. 2).

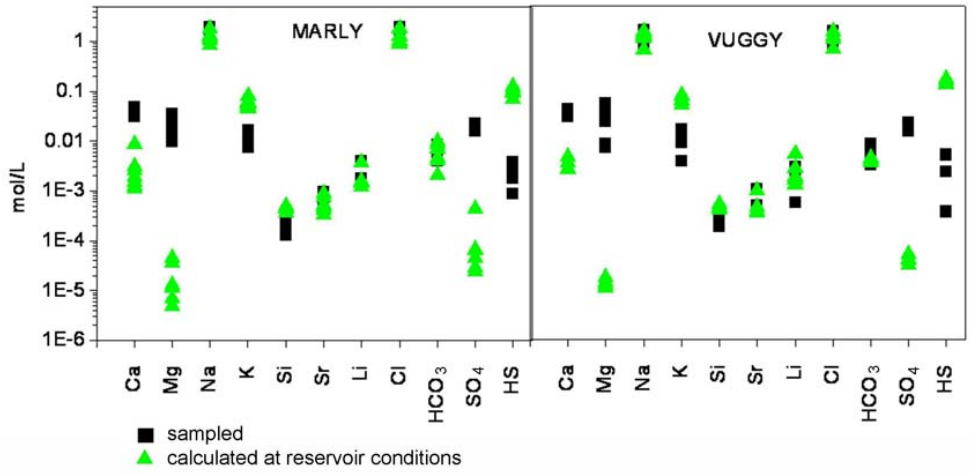

Fig. 2 - Comparison between the chemical composition of calculated at reservoir conditions and the sampled pre-injection composition of Marly and Vuggy waters.

RECONSTRUCTION OF THE "PRIMITIVE BRINE" COMPOSITION (60°C, 15 MPA)

Because of the highly variable salinity of the Weyburn waters composition (TDS 36-117 g/L) and the several simplifications and assumptions necessary to model complex systems such that of Weyburn, the chemical composition calculated at reservoir conditions is highly generic. So, we identified possible compositions of the pre-injection reservoir liquid phases ("primitive brine"), for the Marly and Vuggy units. The "primitive" composition was obtained by geochemical modeling, assuming equilibrium conditions for the mineral assemblage with respect to a Na-Cl brine with a Cl/Na ratio similar to that of seawater (Cl/Na = 1.2). A comparison between the chemical composition of the "primitive brine" and that measured before the CO_2 injection shows a good agreement (within 10%) for most analytical species (Fig. 3). The reconstruction of "primitive brine" composition is the starting point to assess the geochemical impact and evolutions of CO_2 into the oil reservoir vs. time and, as main target, to quantify water-gas-rock reactions to medium time (*i.e.* 100 years).

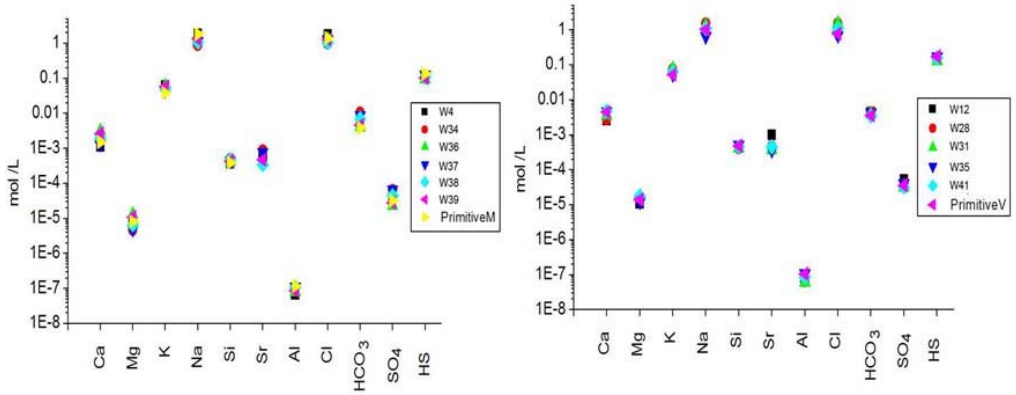

Fig. 3 - Comparison between the calculated "primitive brine" and the sampled pre-injection re-calculated to reservoir composition of the Marly and Vuggy waters.

KINETIC SIMULATION

The modelling of the kinetic aspects of geochemical interaction is indispensable when assessing the temporal evolution of reservoirs subjected to CO_2 injection. While CO_2 dissolution is a process relatively fast, the reaction rates of some minerals (*e.g.* silicate) are so slow that even after hundreds of years equilibrium is not attained. Therefore calculating the amount of CO_2 that can geochemically be trapped, only based on equilibrium assumption, may lead to overestimate the real amount after a certain span of time. The kinetic modelling of impact of the CO_2 injection on Weyburn reservoir is performed for a time of 100 years, adding new kinetic equations and specific surfaces area (SA), for some listed minerals (Table 1) to the standard PHREEQC kinetic database and modifying CO_2 supercritical fugacity and solubility (Duan *et al.*, 1992; Duan & Sun, 2002) under reservoir conditions (7.4 Mpa).

Thermo-kinetic modelling of the temporal evolution of CO_2-rich Weyburn brine interacting with the host-rock minerals, performed over 100 years after the injection, shows for both reservoirs calcite dissolution, while dissolution/precipitation of K-feldspar and kaolinite and precipitation of chalcedony occurs. Dolomite and pyrite reactions can be considered negligible. Dawsonite, albite and muscovite

precipitate as secondary minerals. The pH calculated decreases from 6.91 to 5.14 and from 6.76 to 5.23 for the Marly and Vuggy Units, respectively.

Table 1 - Mineralogical composition of the Marly and Vuggy reservoirs used for the modeling, the specific surface area and the sources of kinetic rate data (* = secondary minerals).

Mineral phase	% w/w		Specific surface area (m^2/g)		Reference
	Marly	Vuggy	Marly	Vuggy	
Calcite	14.5	93.5	0.034	0.015	Plummer *et al.*, 1978
K-feldspar	1.25	0.5	0.175	0.015	Sverdup, 1990
Dolomite	80	3	0.105	0.014	Palandri & Kharaka, 2004
Kaolinite	0.25	0	2.317	0.015	
Chalcedony	0.5	0.5	0.038	0.015	
Pyrite	0.5	0.5	0.012	0.008	
Gypsum	3	0	0.003	-	
Anhydrite	0	2	-	0.013	
Dawsonite*	0	0	0.140	0.140	
Magnesite*	0	0	0.100	0.100	
Muscovite*	0	0	0.106	0.106	
Albite*	0	0	0.115	0.115	
Chlorite*	0	0	0.113	0.113	

DISCUSSION

Geochemical modelling applied to deep CO_2 storage reservoirs (>800 m) is an important tool to define equilibrium conditions among the various phases and to investigate the short- to long-term consequence of CO_2 injection. Since many geochemical parameters of the deep fluids cannot be measured *in-situ*, an *a posteriori* procedure must be used, involving the experimental semi-reliable analytical data. In this work, a new geochemical approach has been used and capable of: i) reconstructing the in-situ reservoir chemical composition, ii) identifying a possible composition of the initially reservoir liquid phases pre-injection, and iii) simulating the system evolution after CO_2 injection.

Because of the chemical complexity of water-CO_2-rock interaction processes in deep reservoirs, numerous uncertainties and approximations characterise the geochemical modelling of these systems. In order to demonstrate that numerical simulations can describe suitably physical-chemical processes of CO_2 storage, these have to be validated through comparison whit field observation.

Validation of geochemical model

To validate our geochemical model simulations of i) the impact of CO_2 injection into the Weyburn reservoir for the period 2000-2003, through kinetically controlled reactions, and ii) the uprising of the reservoir waters at the surface (temperature, pressure and boundary conditions) within the well, have been performed.

The comparison of the simulations results with the real analytical data sampled at well-head in September 2003 shows a good correspondence, within 16 % for most analytical species (Fig.4), with the exception of Ca and Mg. The measured Ca and Mg contents are 1-3 order of magnitude higher than those calculated, suggesting complexation effect likely due to carboxylic acid (Kharaka *et al.*, 2006), not considered in our simulations.

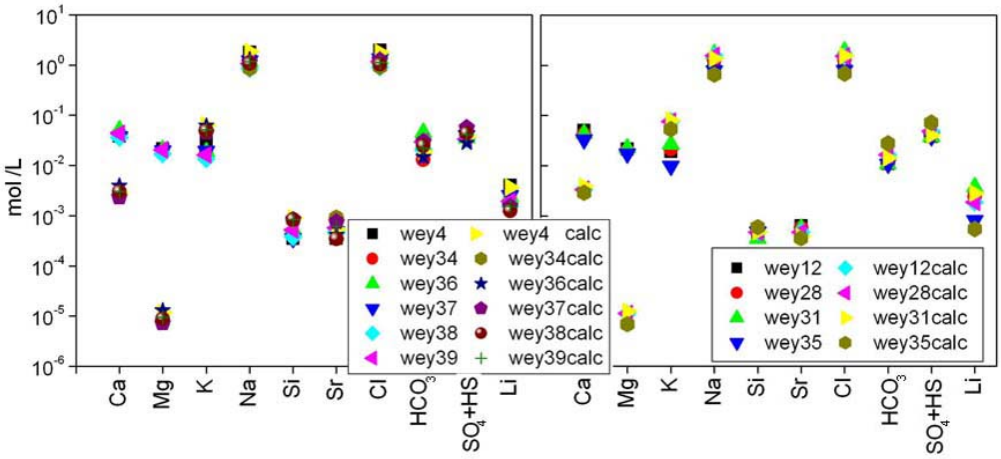

Fig. 4 - Comparison between the 2003 analytical and calculated data for the waters from Marly (left) and Vuggy (right) units.

In order to statically validated our geochemical model we have compared the computed and measured data of September 2003 by using the Median Test with a significant level of $\alpha = 0.05$. The results of Median Test show that the proposed geochemical model is able to reliably describe with a statistical error of < 5% the behaviour of pH, HCO_3, Cl, Li, Na, Sr, Si and $HS+SO_4$, with the exception of Ca, Mg, and K. The simulated K contents result 2 times higher than this analytical, probably due to the overestimation of the K-feldspar kinetic reaction rate.

Geochemical impact of CO_2 injection after 100 years

Kinetic modeling of temporal evolution of Weyburn reservoirs subjected to CO_2 injection, performed over 100 years, shows that "solubility trapping" is prevailing in the early stage, with an amount of dissolved CO_2 of 0.76 moles/L and 0.87 moles/L for Marly and Vuggy units, respectively (Fig. 5). A smaller volume of injected CO_2 is trapped as ions and carbonate complexes (*e.g.* HCO_3, $NaHCO_{3(aq)}$, $CaHCO_{3(aq)}$; 0.1394 mol/L and 0.1801 mol/L for Marly and Vuggy, respectively). After 100 years part of the injected CO_2 is mineralogically trapped as dawsonite (0.027 mol/L and 0.002 mol/L for Marly and Vuggy units, respectively). Such process is catalyzed by high ambient Na concentration, plume-induced CO_2 aqueous saturation, and dissolution of K-feldspar. The mass balance, calculated as difference between dissolved (calcite and dolomite) and precipitated carbonate (dawsonite) minerals, shows that 0.019 and 5.69×10^{-5} mol/L for Marly and Vuggy units, respectively, are effectively trapped after 100 years after the injection. After this period dawsonite is still precipitating, whereas calcite and dolomite are stable, it is highly likely that mineral trapping can increase, extending simulation time to 1000-250000 years (Azaroual *et al.*, 2004).

CONCLUSIONS

Major conclusions that can be drawn are as follows: i) the reconstructed in-situ reservoir (62 °C and 15 MPa) chemical composition shows calcite and dolomite precipitation, while pH increases. Gypsum and anhydrite dissolve and SO_4 reduces to HS; ii) the thermo-kinetic model results partially validated by field observation and statistical Median Test with a statistical error < 5% for most analytical

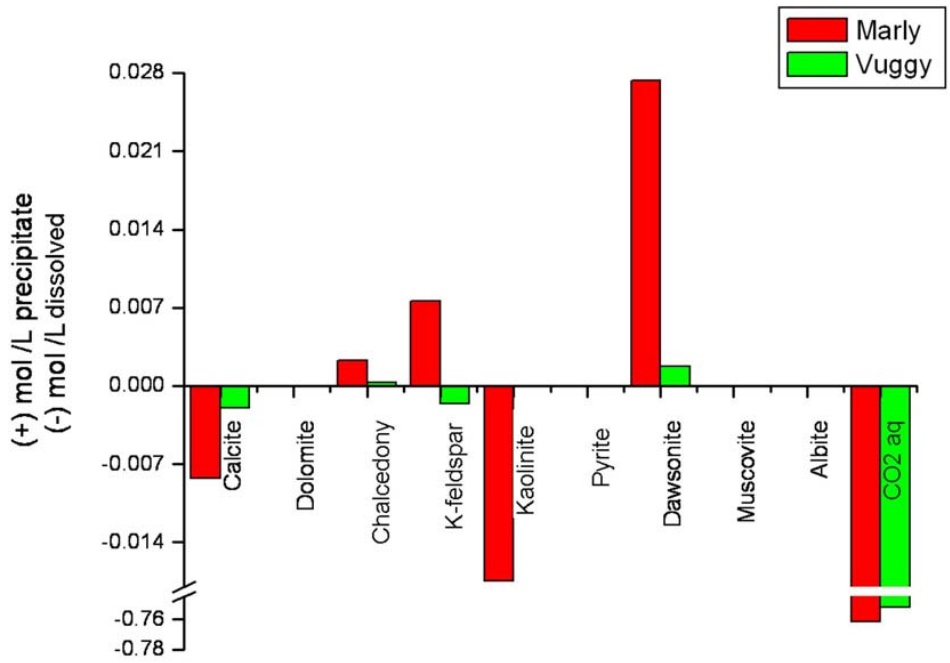

Fig. 5 - Comparison of the mineralogical changes at reservoir conditions (62°C, 15 MPa) due to CO_2 injection after 100 years of kinetic calculation.

species, iii) temporal evolution of Weyburn reservoirs subjected to CO_2 injection suggests that CO_2 can be safety neutralized by solubility (as $CO_{2(aq)}$) and mineral trapping (through dawsonite precipitation).

Despite the experimental data-set available, both the intrinsic limitations and assumptions of geochemical modelling that can introduce a large uncertainty in the results, the proposed method and the kinetic approach are very promising. We can therefore hypothesize to extend or to apply the present model to other geological reservoirs in the world. In order to verify the potentially suitable CO_2 storage reservoirs in Italy an electronic database has been created and containing information about the nature and the thickness of geological formations, the presence of fresh, saline or brackish water, brine, gas and oil, the underground temperature, the permeability, porosity and geochemical characteristics.

The data of 1700 public-available wells drilled on Italian territory for gas/oil and geothermal exploration have been extracted from the paper archives of the Italian Ministry for the Economic Development. This database will constitute the base to apply the presented model to Italian situation in the next future.

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